

# PATENT ABSTRACTS OF JAPAN

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## (54) CERAMIC SLIDING MEMBER AND ITS PRODUCTION

### (57)Abstract:

PURPOSE: To easily obtain in high productivity and yield a ceramic sliding member by providing the surface of a ceramic sintered compact with a diamond or diamond carbon coating film of high adhesiveness.

CONSTITUTION: This ceramic sliding member is such that the surface of a ceramic sintered compact consisting mainly of silicon nitride or SIALON is provided with a diamond or diamond carbon coating film. In this case, the Ca concentration in the region from the surface of the ceramic sintered compact bearing the coating film to a depth of 100 $\mu$ m is lower than that inside this region.

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**CLAIMS**

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[Claim(s)]

[Claim 1] Slide member made from ceramics to which calcium concentration in at least 100-micrometer field of the depth is characterized by decreasing rather than calcium concentration in the interior from this field from the front face of the ceramic sintered compact with which this coat was prepared in the slide member made from ceramics which prepared the coat of diamond or diamond-like carbon on the front face of the ceramic sintered compact which makes silicon nitride or sialon a principal component.

[Claim 2] The manufacture method of the slide member made from ceramics characterized by forming the coat of diamond or diamond-like carbon in the front face after disappearing or decreasing calcium component in at least 100-micrometer field of the depth from the front face of a ceramic sintered compact by heat-treating in a vacuum the ceramic sintered compact which makes silicon nitride or sialon a principal component.

[Claim 3] The manufacture method of the slide member made from ceramics according to claim 2 characterized by heat-treating in the vacuum of 10<sup>-3</sup> or less Pa.

[Claim 4] The manufacture method of the slide member made from ceramics according to claim 2 or 3 characterized by heat-treating at the temperature of 1100-1400 degrees C for 2 to 6 hours.

[Claim 5] The manufacture method of the slide member made from ceramics according to claim 2 to 4 characterized by for the silicon nitride or sialon powder which is the start raw material of a ceramic sintered compact converting calcium compound into calcium, and containing it 1 ppm - 1% of the weight.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the slide member made from ceramics which prepared the coat of diamond or diamond-like carbon in the front face of the base material which consists of a ceramic sintered compact, and its manufacture method.

[0002]

[Description of the Prior Art] While ceramics are high degrees of hardness, it excels in thermal resistance and abrasion resistance, and since it excels also in mechanical properties, such as intensity, toughness, and a thermal shock resistance, the ceramics which make especially silicon nitride or sialon a principal component are widely used as slide member of a cutting tool, an abrasion-resistant tool, and others.

[0003] In order to raise the reliability and the life of these ceramics further in recent years, as an enveloping layer, a degree of hardness is very high, and is chemically stable, preparing the coat of the diamond excellent in sliding-proof abrasiveness or diamond-like carbon attracts attention, and the research and development are briskly done in many fields. However, the coat which consists of diamond or diamond-like carbon has the fault that adhesion with ceramics is low and a coat tends to exfoliate.

[0004] As an attempt which raises the adhesion to the ceramics of a diamond or diamond-like carbon coat, an alumimium nitride film is covered to cemented carbide or a ceramic sintered compact, and forming a diamond or a hard-carbon coat on it is proposed by JP,5-214532,A. Moreover, using the titanium-nitride film of a non-stoichiometric composition is indicated by JP,4-254584,A as an interlayer between cemented carbide, a ceramic sintered compact, a diamond, or a hard-carbon coat.

[0005] However, when the matter which is dissolving carbon like a tungsten carbide or a titanium carbide as a reason whose adhesion of a diamond or a hard-carbon coat improves by using alumimium nitride for an interlayer in JP,5-214532,A is a base material, although it is because the carbonaceous diffusion and carbonaceous dissolution which are produced during coat formation can be prevented, concrete explanation is not made about the case of ceramic sintered compacts, such as silicon nitride in which a base material does not contain carbon.

[0006] Moreover, in JP,4-254584,A, by a titanium carbide's becoming close to a stoichiometric composition by carbonaceous diffusion by the interface with a diamond or a hard-carbon coat by preparing the titanium-carbide film of the non-stoichiometric composition which reduced the carbon content as an interlayer, therefore carbonaceous diffusion stopping at a base-material side, since a titanium carbide continues being a non-stoichiometric composition, a big volume change is not produced but it is said that adhesion with a base material improves.

[0007] On the other hand, after processing the front face of the sintered compact which makes silicon nitride a principal component with an acid or alkali, forming a diamond or diamond-like carbon coat is indicated by JP,4-202075,A. Since the grain boundary of a silicon nitride sintering body surface and the holohyaline near the grain boundary are corroded preferentially, the pillar-shaped particle of silicon nitride remains, and detailed irregularity is formed and the rate of area of surface silicon nitride

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increases by processing with an acid or alkali, the coefficient of thermal expansion on the front face of a base material becomes still closer to a diamond, and it is indicated that high adhesion is obtained.

[0008]

[Problem(s) to be Solved by the Invention] However, also in the above-mentioned conventional method, it was difficult to fully raise adhesion with a ceramic sintered-compact, diamond, or diamond-like carbon coat. That is, by the method of preparing interlayers, such as aluminum nitride and a titanium carbide, the number of times of covering and the number of coats are made increased by an interlayer's formation, and possibility that ablation will arise among both interlayers and between the coats of interlayer, diamond, or diamond-like carbon becomes high.

[0009] Moreover, by the method of processing a ceramic sintered compact with an acid or alkali, improvement in adhesion to the extent that it is difficult to form the coat of diamond or diamond-like carbon in accordance with the shape of toothing with a detailed front face, a coat does not fully turn to the interior of the hole in which the glass phase of a grain boundary began to melt into, and was formed, therefore it is expected is not obtained.

[0010] Furthermore, since fluoric acid, a FUSU nitric acid, or a sodium hydroxide is used in the case of the method of processing a ceramic sintered compact with an acid or alkali, not only these managements but the correspondence safety and in respect of environment is needed. In addition, the glass phase of a ceramic sintered compact may melt too much, or it is necessary to also manage the corrosion-treatment conditions by the acid or alkali strictly, when melt and there is too nothing, the fall of adhesion may be caused, and thereby, reduction in the yield may be caused.

[0011] this invention aims at offering the method of being an easy method and forming offering the slide member made from ceramics which equipped the front face of a ceramic sintered compact with the coat of the diamond excellent in adhesion, or diamond-like carbon in view of this conventional situation, and this slide member made from ceramics with sufficient productivity by the high yield.

[0012]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, slide member made from ceramics which this invention offers is characterized by decreasing rather than calcium concentration [ in / the interior / from this field / in calcium concentration in at least 100-micrometer field of the depth ] from the front face of the ceramic sintered compact with which it is the slide member made from ceramics which prepared the coat of diamond or diamond-like carbon, and this coat was prepared on the front face of the ceramic sintered compact which makes silicon nitride or sialon a principal component.

[0013] The manufacture method of the slide member made from ceramics of this invention is characterized by disappearing or decreasing calcium component in at least 100-micrometer field of the depth from the front face of a ceramic sintered compact, and forming the coat of diamond or diamond-like carbon in the front face the back by heat-treating in a vacuum the ceramic sintered compact which makes silicon nitride or sialon a principal component.

[0014] In addition, the diamond-like carbon said here is amorphous, and means a diamond and the carbon which has an analogous property, and Diamond-like carbon is called in English.

[0015]

[Function] In this invention, adhesion with the coat of ceramic sintered-compact, diamond, or diamond-like carbon was able to be raised by paying one's attention to the impurity of the minute amount contained in the silicon nitride powder which is the raw material of the ceramic sintered compact which makes silicon nitride or sialon a principal component, especially a lime compound, and disappearing or decreasing a lime compound from a sintering body surface or its near.

[0016] Namely, the ceramic sintered compact which makes a principal component silicon nitride ( $\text{Si}_3\text{N}_4$ ) or sialon ( $\text{SiAlON}$ ) Although manufactured by carrying out addition mixture and sintering a sintering acid to this using the silicon nitride powder of marketing which has a suitable particle size, purity, a rate of alpha, an aspect ratio, etc. according to the use made into the purpose The impurity of a minute amount, for example, oxygen, carbon, chlorine, iron, calcium, aluminum, etc. are contained in silicon nitride powder in addition to  $\text{Si}_3\text{N}_4$ .

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[0017] These impurities are very difficult for being what is mixed from the facility used in case silicon nitride powder is produced, a fixture, etc., or already being contained in the solid-state and liquid as a raw material for producing silicon nitride powder, and losing this all completely.

[0018] Therefore, the ceramic sintered compact which makes silicon nitride or sialon a principal component contained these impurities, and when X-ray analysis was performed about the front face and interior, it made it clear that  $\text{Y}_2\text{O}_3\text{-N}_4\text{Si}_3\text{O}_{12}$  and calcium(Fe, Mg)  $\text{Si}_2\text{O}_6$  are formed in any part. Moreover, although these compounds remained in the sintering inside-of-the-body section when this ceramic sintered compact was heat-treated in the vacuum, in a sintering body surface, only  $\text{Y}_2\text{O}_3\text{-N}_4\text{Si}_3\text{O}_{12}$  remained, and it turns out that calcium(Fe, Mg)  $\text{Si}_2\text{O}_6$  disappears.

[0019] Then, when the diamond coat and the diamond-like carbon coat were formed in the front face, respectively and the adhesion was evaluated by the pin-ON-disk test method about the ceramic sintered compact beforehand heat-treated in the vacuum, and the ceramic sintered compact which does not perform this heat treatment, the ceramic sintered compact beforehand heat-treated in the vacuum showed one about 3 times the adhesion of this compared with the sintered compact without heat treatment.

[0020] Although this reason is not clear, it can think as the following. As shown in Table 1, in combination with oxygen, calcium and Mg have high ionic bond nature, and bonding strength's is [ Mg ] weaker than Si. Therefore, if it heat-treats in a vacuum, in order that calcium and Mg with high ionic bond nature may disappear from a ceramic sintering body surface, ionic bond nature becomes weak and, as for near the sintering body surface, covalent-bond nature becomes high.

[0021]

[Table 1]

Origin Base Ionic bond nature (%) Strength Si of single bond (kJ/mol) 37 444calcium 62 134Mg 55 155

[0022] Moreover, both diamond and diamond-like carbon is  $\text{sp}^3$  hybrid orbitals, and it is known that covalent-bond nature is shown. For this reason, the formation of a coat excellent in adhesion is considered to have become possible by combining more strongly than the sintering body surface which shows ionic bond nature with the high sintering body surface of covalent-bond nature the coat of the diamond in which covalent-bond nature is shown, or diamond-like carbon.

[0023] in addition, sintering after heat-treating in a vacuum to the sintered compact which makes silicon nitride or sialon a principal component -- with evaluation of the elemental analysis of  $\text{Y}_2\text{O}_3\text{-N}_4\text{Si}_3\text{O}_{12}$  in the living body and calcium(Fe, Mg)  $\text{Si}_2\text{O}_6$  The result which evaluated the adhesion of the coat of diamond or diamond-like carbon by the pin-ON-disk examining method, In order to excel adhesion in case the adhesion at the time of heat-treating in a vacuum does not heat-treat, it turns out that the concentration distribution of calcium(Fe, Mg)  $\text{Si}_2\text{O}_6$ , i.e., the concentration distribution of calcium component, needs to be decreasing from a field with a depth of at least 100 micrometers from the front face of a sintered compact.

[0024] Heat treatment in the vacuum for obtaining improvement in the adhesion of the diamond based on disappearance or reduction of this calcium component or a diamond-like coat is preferably performed in the vacuum of 10<sup>-3</sup> or less Pa. An oxide film is formed in a sintering body surface, and since it becomes difficult for calcium and Mg component to dissipate from a sintering body surface also with heat treatment, it becomes impossible to expect the effect of this invention in the case of the pressure to which the atmosphere at the time of heat treatment exceeds ten to 3 Pa.

[0025] As for the conditions of heat treatment in a vacuum, it is desirable to carry out at the temperature of 1100-1400 degrees C for 2 to 6 hours. In the temperature of less than 1100 degrees C, or less than 2 heat treatment hours, a sintering body surface is not effectively reformed for this condition, and the adhesion of a diamond or diamond-like carbon coat does not improve enough. On the contrary, it is because there is a possibility that silicon nitride may sublime, in heat treatment time exceeding the temperature exceeding 1400 degrees C, or 6 hours.

[0026] Moreover, what is necessary is it to be possible to crystallize the grain-boundary phase of the sintered compact which makes silicon nitride or sialon a principal component, and just to adjust the temperature of heat treatment, and the pattern of time by performing heat treatment in this vacuum, if needed in that case. By crystallization of the grain-boundary phase by this heat treatment, the intensity in

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the elevated temperature of a sintered compact improves.

[0027] In this invention, ceramic sintered compacts are ceramics which make silicon nitride or sialon a principal component, and other ceramic components (SiC), for example, silicon carbide, the zirconia (ZrO<sub>2</sub>), the titanium carbide (TiC), the hafnium carbide (HfC), etc. may be contained. Moreover, whiskers, such as a silicon carbide whisker, a silicon nitride whisker, and a carbon whisker, may be included.

[0028] An impurity is contained in the powder raw material of the ceramic sintered compact which makes silicon nitride or sialon a principal component like the above, and the content changes with the manufacture method of silicon nitride powder, such as direct nitriding and the imido decomposing method, or powdered refinement methods. It is desirable that calcium content of an impurity is in 1 ppm - 1% of the weight of the range especially at the well which attains the effect of this invention although it is 0.5 ppm - about 2 % of the weight with the content of calcium, therefore commercial silicon nitride powder. It is because a sintered compact sufficiently precise as slide member will no longer be obtained if the improvement effect in adhesion of the coat by heat treatment of this invention among a vacuum becomes remarkable and exceeds 1 % of the weight, when calcium content in a sintered compact is 1 ppm or more.

[0029] Although a sintering acid is added and sintered at silicon nitride powder in manufacture of the ceramic sintered compact which makes silicon nitride or sialon a principal component, naturally the ceramic sintered compact of this invention may contain the sintering acid. As this sintering acid, a yttrium oxide (Y<sub>2</sub>O<sub>3</sub>), an aluminum oxide (aluminum 2O<sub>3</sub>), aluminum nitride (AlN), a zirconium oxide (Zr 2O<sub>3</sub>), a magnesium oxide (MgO), an erbium oxide (Er 2O<sub>3</sub>), an oxidation dysprosium (Dy 2O<sub>3</sub>), titanium oxide (TiO<sub>2</sub>), silicon oxide (SiO<sub>2</sub>), a ytterbium oxide (Yb 2O<sub>3</sub>), etc. can be mentioned, for example.

[0030] A ceramic sintering body size is not limited but may have also about a configuration the shape of the shape of a pillar, a cylinder, and hollow, the configuration which has the pore section, and what other complicated configurations. This ceramic sintered compact can also perform polish, wrapping processing, etc. in advance of formation of a coat according to the purpose of use.

[0031] Although all well-known methods can be used in order to form the coat of diamond or diamond-like carbon on the front face of the ceramic sintered compact which makes a principal component the silicon nitride or sialon which performed heat treatment in the above-mentioned vacuum, especially, using vapor phase synthetic methods, such as various CVD, a combustion flame method, the ion plating method, and the sputtering method, reaches practically, and it is desirable on production.

[0032] A vapor phase synthetic method excites the material gas containing carbon source gas in a reaction chamber, and makes the coat of diamond or diamond-like carbon specifically form on a sintered compact. As carbon source gas, it is used if needed using the carbon compounds containing nitrogen besides various hydrocarbons, a halogen, oxygen, etc., or such mixture, mixing with hydrogen, an argon, helium, etc. As the excitation method of material gas, there are RF plasma CVD method, DC plasma CVD method, a microwave plasma CVD method, heat filament CVD, heat CVD, a plasma flash method, and a thermal-plasma method.

[0033]

[Example]

Si<sub>3</sub>N<sub>4</sub> powder of the particle size (median size which is a median) shown in the example 1 following table 2, and marketing with an impurity content was used, 5 % of the weight of 2OY<sub>3</sub> powder of 1.1 micrometers of mean particle diameters and 3 % of the weight of 2Oaluminum<sub>3</sub> powder of 0.6 micrometers of mean particle diameters were added to this, and wet blending by the ball mill was performed in ethanol for 100 hours.

[0034]

[Table 2]

Character of silicon nitride powder Median size \*\* Pure Object \*\* \*\* Amount (micrometer) aluminum  
O C calcium Fe Cl Mg 0.9 20ppm 1.2wt% 0.1wt% 0.2wt% 20ppm 15ppm 0.01wt% [0035] After drying  
this end of mixed powder, CIP fabrication was carried out by the pressure of 5000 kg/cm<sup>2</sup>. Heating

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maintenance of the obtained Plastic solid was carried out at 1600 degrees C in the nitrogen gas atmosphere of one atmospheric pressure for 4 hours, next, sintering of 6 hours was performed at 1700 degrees C, and HIP processing of 2 hours was performed to the obtained sintered compact in the nitrogen gas atmosphere of 1700 degrees C and 500 atmospheric pressure.

[0036] After carrying out wrapping processing of the silicon nitride sintered compact obtained in this way, it has arranged in a vacuum-heat-treatment furnace. Next, evacuation of the inside of a furnace was carried out to ten to 3 Pa, and the vacuum heat treatment which holds a test piece at 1300 degrees C for 3.5 hours was given. RF plasma CVD method was used for the front face of the sintered compact which gave this vacuum heat treatment, the diamond-like carbon coat with a thickness of 1.1 micrometers was formed in it, and it considered as the test piece 1. Using methane as material gas, the membrane formation conditions of a diamond-like carbon coat are pressure 0.5Torr(s), and were set to output power 800W.

[0037] Moreover, the comparison test piece 1a which heat-treated in nitrogen atmosphere and formed the diamond-like carbon coat, the comparison test piece 1b which did not perform a vacuum heat treatment but formed the diamond-like carbon coat on the same conditions, and the comparison test piece 1c which perform only wrapping processing and do not have a diamond-like carbon coat produced instead of heat-treating in a vacuum, after carrying out wrapping processing of the silicon-nitride sintered compact manufactured like the above for comparison. In addition, the heat treatment conditions in the inside of nitrogen atmosphere were made into 5 hours at the same 1300 degrees C as the case in a vacuum, and processed with atmospheric pressure.

[0038] According to the pin-ON-disk test method, the sliding examination was performed using these test pieces 1 and the comparison test pieces 1a, 1b, and 1c on the conditions of 150mm/second in 20 Ns of loads, and sliding speed, and the 50000 number of times of sliding. Consequently, although coefficient of friction was 0.9 in comparison test piece 1c without a diamond-like carbon coat, both the test piece 1 of this invention, test piece heat-treated in nitrogen atmosphere 1a, and comparison test piece 1b that formed the diamond-like carbon coat, without performing heat treatment were 0.2.

[0039] However, when the wear depth was seen, in the test piece 1 of this invention, it was far [ as 0.8 micrometers ] few to comparison test piece 1c being 8 micrometers, and the comparison test pieces 1a and 1b being 3 micrometers. Moreover, although exfoliation of a diamond-like carbon coat was accepted in comparison test piece 1a which carried out coat formation, and comparison test piece 1b which carried out coat formation without heat treatment after heat-treating in nitrogen atmosphere, exfoliation of a coat was not accepted in the test piece 1 of this invention. From these results, it became clear that the adhesion of a coat improves remarkably with the test piece 1 of this invention in which the diamond-like carbon coat was formed after the vacuum heat treatment.

[0040] On the other hand, it was the same silicon nitride sintered compact as the above, and the element distribution in a grain-boundary phase was investigated about the depth direction, using an X-ray microanalyser (EPMA) about the sintered compact which heat-treated in the vacuum according to this invention, and the sintered compact which has not performed the sintered compact and heat treatment which heat-treated in nitrogen atmosphere, and the result was shown in drawing 1. Drawing 1 is a graph which shows the distribution of Y20-N4Si 12O48 in the depth direction, and calcium(Fe, Mg) Si 2O6 from a sintering body surface, and the vertical axis is expressed as the relative graduation which set to 100 the content of Y20-N4Si 12O48 in the front face in the sintered compact which gave the vacuum heat treatment.

[0041] That Y20-N4Si 12O48 and calcium(Fe, Mg) Si 2O6 are a fixed distribution to both the depth directions, and heat treatment in nitrogen atmosphere is ineffective made clear the sintered compact which has not performed the sintered compact and heat treatment which heat-treated in nitrogen atmosphere so that drawing 1 might show. On the other hand, although both compounds existed in the interior in the sintered compact which heat-treated in the vacuum, calcium(Fe, Mg) Si 2O6 began reduction gradually toward a depth of about 400 micrometers to the front face from the front face, and was not detected at all on a front face.

[0042] Moreover, using the transverse test piece which consists of the same sintered compact as an

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example 1, heat treatment in a vacuum or heat treatment in nitrogen atmosphere was performed on the same conditions as the above, and the 1.1-micrometer diamond-like carbon coat was formed in these test pieces and the test piece which is not heat-treated by the plasma CVD method on the same conditions after wrapping processing.

[0043] Anti-\*\*\*\* (ordinary temperature, 600 degrees C, 800 degrees C, 900 degrees C, 1000 degrees C, 1100 degrees C, 1200 degrees C, and 1300 degrees C) was measured using each test piece which prepared these diamond-like coats. The result is shown in drawing 2. The test piece which performed heat treatment in a vacuum had small degradation of most anti-\*\*\*\* also in the elevated temperature, and the test piece which performed heat treatment in nitrogen atmosphere showed what has not heat-treated, and the temperature dependence which seldom changes so that this result might show.

[0044] Furthermore, although the peak which originates in the grain-boundary phase of a crystalline substance in addition to the pattern of silicon nitride had appeared in the test piece which performed heat treatment in a vacuum when crystal structure diffraction of each [ these ] test piece was investigated, in the test piece heat-treated in nitrogen atmosphere, the peak by the grain-boundary phase of a small deer crystalline substance had not appeared other than the pattern of silicon nitride. Moreover, only the peak of silicon nitride was detected in the test piece which is not heat-treating. The adhesion of a diamond-like carbon coat not only improves, but from these results, it can raise an elevated-temperature property by crystallization of a grain-boundary phase by heat-treating in a vacuum.

[0045] Si<sub>3</sub>N<sub>4</sub> powder of the particle size (median size which is a median) shown in the example 2 following table 3, and marketing with an impurity content was used, 10 % of the weight of SiC whiskers with a length of 5-50 micrometers was added to this by 6 % of the weight of 2OEr<sub>3</sub> powder of 0.8 micrometers of mean particle diameters, 3 % of the weight of AlN powder of 1.1 micrometers of mean particle diameters, and 0.4-2 micrometers of minor axes, wet blending was carried out to it like the example 1, and it dried.

[0046]

[Table 3]

Character of silicon nitride powder Median size \*\* Pure Object \*\* \*\* Amount (micrometer) aluminum  
O C calcium Fe Cl Mg 1.5 30ppm 2.1wt% 0.1wt% 0.6wt% 60ppm 29ppm 0.01wt% [0047] Hotpress  
sintering was performed for this end of mixed powder on 200 atmospheric pressure, 1750 degrees C, and the conditions of 2 hours, and the silicon nitride sintered compact was manufactured. After carrying out wrapping processing of the silicon nitride sintered compact obtained in this way, it has arranged in a vacuum-heat-treatment furnace, evacuation of the inside of a furnace was carried out to ten to 4 Pa, and the vacuum heat treatment of 2.5 hours was performed at 1400 degrees C.

[0048] RF plasma CVD method was used for the front face of the sintered compact which gave this vacuum heat treatment, the diamond-like carbon coat with a thickness of 0.6 micrometers was formed in it, and it considered as the test piece 2 of this invention. Using methane as material gas, the membrane formation conditions of this diamond-like carbon coat are pressure 0.8Torr(s), and were set to output power 600W.

[0049] Moreover, after carrying out wrapping processing of the silicon nitride sintered compact manufactured like the above for comparison, a vacuum heat treatment was not performed but comparison test piece 2a which formed the diamond-like carbon coat on the same conditions, and comparison test piece 2b which performs only wrapping processing and does not form a diamond-like carbon coat were produced.

[0050] The sliding examination was performed on the same conditions as an example 1 using these test pieces 2 and the comparison test pieces 2a and 2b. Consequently, although coefficient of friction was 1.3 in comparison test piece 2b without a diamond-like carbon coat, both comparison test piece 2a that carried out coat formation, without performing the test piece 2 and vacuum heat treatment of this invention was 0.2.

[0051] However, when the wear depth was seen, as for the test piece 2 of this invention, 9 micrometers and comparison test piece 2a had little comparison test piece 2b to being 2 micrometers as far as 0.4 micrometers, and although exfoliation of a diamond-like carbon coat was accepted in comparison test

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piece 2a which moreover carried out coat formation without the vacuum heat treatment, exfoliation of a coat was not accepted in the test piece 2 of this invention. From these results, it became clear that the adhesion of a coat is improving remarkably with the test piece 2 of this invention in which the diamond-like carbon coat was formed after the vacuum heat treatment.

[0052] After carrying out the grinding process of the silicon nitride sintered compact manufactured like example 3 example 2, it has arranged in a vacuum-heat-treatment furnace, evacuation of the inside of a furnace was carried out to ten to 4 Pa, and the vacuum heat treatment of 4 hours was performed at 1200 degrees C. RF plasma CVD method was used for the front face of the sintered compact which gave this vacuum heat treatment, the diamond coat with a thickness of 5 micrometers was formed in it, and pin-ON-disk test piece 3a was produced. Moreover, after carrying out the grinding process of the silicon nitride sintered compact manufactured like the above for comparison, comparison test piece 3b which formed the diamond coat on the same conditions was produced, without performing a vacuum heat treatment.

[0053] The same sliding examination as examples 1 and 2 was performed using these test pieces 3a and 3b. Consequently, although exfoliation of a diamond coat was not accepted in test piece 3a by this invention, big exfoliation was seen in comparison test piece 3b. This result showed that the adhesion of a coat was improving in test piece 3a of this invention in which the diamond coat was formed after the vacuum heat treatment.

[0054] Moreover, the distribution of Y2O-N4Si 12O48 in the depth direction and calcium(Fe, Mg) Si 2O6 was measured like the example 1 from the front face of a sintered compact about these test pieces 3a and 3b. Consequently, although both compounds existed in the interior of test piece 3a of this invention, calcium(Fe, Mg) Si 2O6 began reduction gradually toward a depth of about 350 micrometers to the front face from the front face, and was not detected at all on a front face. On the other hand, in comparison test piece 3b, it became clear that both compounds are fixed distributions to the depth direction.

[0055] Si3N4 powder of two kinds of marketing was used, 4 % of the weight of 2Oaluminum3 powder of 0.8 micrometers of mean particle diameters, 4 % of the weight of AlN powder of 1.0 micrometers of mean particle diameters, and 3 % of the weight of 2OY3 powder of 0.8 micrometers of mean particle diameters were added to each Si3N4 powder, and wet blending with the particle size (median size which is a median) shown in the example 4 following table 4, and an impurity content by the ball mill was performed in ethanol for 100 hours.

[0056]

[Table 4]

Character of silicon nitride powder Powder Median size \*\* Pure Object \*\* \*\* Amount Kind

(micrometer) aluminum O C calcium Fe Cl Mg A 0.7 30ppm 2.5wt% 0.1wt% 0.1wt% 50ppm 18ppm

0.01wt% B 0.7 28ppm 2.6wt% 0.13wt% 1.5wt% 47ppm 18ppm 0.01wt%[0057] After drying this end of mixed powder, CIP fabrication was carried out by the pressure of 5000 kg/cm2. Heating maintenance of the obtained Plastic solid was carried out at 1600 degrees C in the nitrogen gas atmosphere of one atmospheric pressure for 4 hours, next, sintering of 5 hours was performed at 1800 degrees C, and HIP processing of 2 hours was performed to the obtained sintered compact in the nitrogen gas atmosphere of 1750 degrees C and 1000 atmospheric pressure.

[0058] When the organization observation of each silicon nitride sintered compact and density which were obtained in this way were measured, the sintered compact using Powder A did not have a defect, and density is 3.24 g/cm3 and it turns out that it has turned precisely enough. However, as for the sintered compact using Powder B, a front face and the interior had many defects, such as a pore, and density had not turned into 3.11 g/cm3 precisely enough, either.

[0059] Next, the sintered compact manufactured using this powder A was processed into the pin-ON-disk examination, and after carrying out wrapping processing, the vacuum heat treatment was given by arranging in a vacuum-heat-treatment furnace, carrying out evacuation of the inside of a furnace to ten to 3 Pa, and holding on time [ to show a test piece in the following table 5 at 1150 degrees C ] conditions. In this case, the silicon nitride near a front face was sublimating the test piece which

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performed the vacuum heat treatment of 8 hours at 1150 degrees C of conditions 5, and it did not hold the configuration of the test piece before heat treatment.

[0060] RF plasma CVD method was used for the front face of the test piece which gave the vacuum heat treatment from conditions 1 to conditions 4, and the diamond-like carbon coat with a thickness of 1.5 micrometers was formed in it. The pin-ON-disk examination was performed for these test pieces on the same conditions as an example 1, and the result which evaluated the coefficient of friction and the wear depth was collectively shown in Table 5. Moreover, while cutting these test pieces at right angles to an examination side, measuring the concentration change of calcium component to the depth direction from an examination side by EPMA and showing the result in drawing 3, in quest of the depth from the front face of an origin to which calcium concentration falls, it was shown in Table 5.

[0061]

[Table 5]

| Conditions 1                          | Conditions 2                              | Conditions 3        | Conditions 4        | The condition 5                    | holding time (H)          |
|---------------------------------------|---|---------------------|---------------------|------------------------------------|---------------------------|
| 0.5                                   | 1.0                                       | 2.0                 | 5.0                 | 8.0                                | ** ** *                   |
| Charge Number                         | 0.9                                       | 0.8                 | 0.3                 | 0.2                                | - Wear Depth (Micrometer) |
| 2.7                                   | 2.6                                       | 0.8                 | 0.8                 | - ** Film ** ** *                  |                           |
| Exfoliation                           | Exfoliation                               | With no exfoliation | With no exfoliation | -calcium concentration fall origin |                           |
| (micrometer)                          | 30  | 80                  | 110                 | 340                                |                           |
| The silicon nitride near a front face | sublimated on the - (notes) conditions 5. |                     |                     |                                    |                           |

[0062] From these results, when calcium concentration is not falling like conditions 1 and 2 from a part deeper 100 micrometers or more than a sintering body surface When calcium concentration is falling like conditions 3 and 4 to the diamond-like carbon coat having exfoliated from the part deeper 100 micrometers or more than a sintering body surface Exfoliation of a diamond-like coat does not arise but it turns out that the adhesion of a coat is improving, and that the wear depth is also small compared with conditions 1 and 2.

[0063]

[Effect of the Invention] According to this invention, the slide member made from ceramics which could form the coat of the diamond of high adhesion or diamond-like carbon by the yield good productivity and high by the easy method, therefore equipped the front face with the coat of the diamond of high adhesion or diamond-like carbon on the front face of the ceramic sintered compact which makes silicon nitride or sialon a principal component can be offered.

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AP - JP19940168919 19940628

CPY - SUME

DC - L02 P73

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XIC - B32B-018/00 ; C04B-041/87

XP - N1996-094415

AB - J08012471 Ceramic sliding member is made by heat treating a ceramic sintered compact contg. Si nitride or sialon in a vacuum to dissipate or decrease Ca component within of least 10 mum depth from the surface of the sintered compact then forming diamond or diamond-like C film on the surface.

- Used for sliding members having diamond or diamond-like C film.

- (Dwg.0/3)

IW - CERAMIC SLIDE MEMBER MANUFACTURE HEAT TREAT CERAMIC SINTER COMPACT CONTAIN SILICON NITRIDE SIALON VACUUM DISSIPATE CALCIUM COMPONENT FORMING DIAMOND FILM

IKW - CERAMIC SLIDE MEMBER MANUFACTURE HEAT TREAT CERAMIC SINTER COMPACT CONTAIN SILICON NITRIDE SIALON VACUUM DISSIPATE CALCIUM COMPONENT FORMING DIAMOND FILM

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PAW - (SUME ) SUMITOMO ELECTRIC IND CO

TI - Ceramics sliding member mfr. - by heat treating ceramic sintered compact contg. silicon nitride or sialon in vacuum to dissipate calcium component, then forming diamond film

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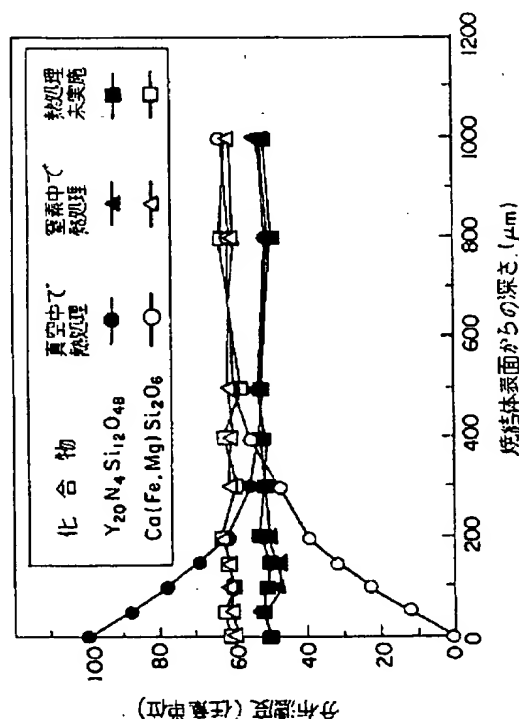
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(54)【発明の名称】 セラミックス製摺動部材及びその製造方法

(57)【要約】

【目的】 セラミックス焼結体の表面に密着性に優れたダイヤモンド又はダイヤモンド状炭素の被膜を備えたセラミックス製摺動部材を、簡単な方法で、生産性良く、且つ高い歩留りで形成し、提供する。

【構成】 窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体の表面上に、ダイヤモンド又はダイヤモンド状炭素の被膜を設けたセラミックス製摺動部材であって、該被膜の設けられたセラミックス焼結体の表面から少なくとも100 $\mu$ mの深さの領域内のCa濃度が、この領域より内部におけるCa濃度よりも減少している。



## 【特許請求の範囲】

【請求項1】 窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体の表面上に、ダイヤモンド又はダイヤモンド状炭素の被膜を設けたセラミックス製摺動部材において、該被膜の設けられたセラミックス焼結体の表面から少なくとも100 $\mu$ mの深さの領域内のCa濃度が、この領域より内部におけるCa濃度よりも減少していることを特徴とするセラミックス製摺動部材。

【請求項2】 窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体を真空中において熱処理することにより、セラミックス焼結体の表面から少なくとも100 $\mu$ mの深さの領域内のCa成分を消失ないし減少させた後、その表面にダイヤモンド又はダイヤモンド状炭素の被膜を形成することを特徴とするセラミックス製摺動部材の製造方法。

【請求項3】 熱処理を10<sup>-3</sup>Pa以下の真空中で行うことを特徴とする、請求項2に記載のセラミックス製摺動部材の製造方法。

【請求項4】 熱処理を1100～1400℃の温度で2～6時間行うことを特徴とする、請求項2又は3に記載のセラミックス製摺動部材の製造方法。

【請求項5】 セラミックス焼結体の出発原料である窒化ケイ素又はサイアロン粉末が、Ca化合物をCaに換算して1ppm～1重量%含んでいることを特徴とする、請求項2～4のいずれかに記載のセラミックス製摺動部材の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、セラミックス焼結体からなる母材の表面にダイヤモンド又はダイヤモンド状炭素の被膜を設けたセラミックス製摺動部材、及びその製造方法に関する。

## 【0002】

【従来の技術】 セラミックスは高硬度であると共に、耐熱性、耐摩耗性に優れ、特に窒化ケイ素又はサイアロンを主成分とするセラミックスは強度、靱性、耐熱衝撃性等の機械的特性にも優れているため、切削工具、耐摩工具、その他の摺動部材として広く利用されている。

【0003】 近年、かかるセラミックスの信頼性並びに寿命を更に向上させるため、被覆層として硬度が極めて高く、化学的に安定であり、耐摺動摩耗性に優れたダイヤモンド又はダイヤモンド状炭素の被膜を設けることが注目され、多くの分野でその研究開発が盛んに行われている。しかし、ダイヤモンド又はダイヤモンド状炭素からなる被膜はセラミックスとの密着性が低く、被膜が剥離しやすいという欠点がある。

【0004】 ダイヤモンド又はダイヤモンド状炭素被膜のセラミックスへの密着性を向上させる試みとして、例えば、特開平5-214532号公報には、超硬合金やセラミックス焼結体に窒化アルミニウム膜を被覆し、そ

の上にダイヤモンド又は硬質炭素被膜を形成することが提案されている。又、特開平4-254584号公報には、超硬合金やセラミックス焼結体とダイヤモンド又は硬質炭素被膜の間の中間層として、非化学量論組成の窒化チタン膜を用いることが記載されている。

【0005】 しかし、特開平5-214532号公報では、中間層に窒化アルミニウムを用いることによりダイヤモンド又は硬質炭素被膜の密着性が向上する理由として、炭化タングステンや炭化チタンのように炭素を固溶している物質が基材である場合には、被膜形成中に生じる炭素の拡散や固溶を防ぐことができるためであるとしているが、基材が炭素を含まない窒化ケイ素等のセラミックス焼結体の場合については具体的な説明がなされていない。

【0006】 又、特開平4-254584号公報においては、中間層として炭素量を低減させた非化学量論組成の炭化チタン膜を設けることにより、ダイヤモンド又は硬質炭素被膜との界面では炭素の拡散により炭化チタンが化学量論組成に近くなり、そのため基材側では炭素の拡散が止まって炭化チタンが非化学量論組成のままであるから、大きな体積変化を生じず、基材との密着性が向上することが述べられている。

【0007】 一方、特開平4-202075号公報には、窒化ケイ素を主成分とする焼結体の表面を酸又はアルカリで処理した後、ダイヤモンド又はダイヤモンド状炭素被膜を形成することが開示されている。酸又はアルカリで処理することにより、窒化ケイ素焼結体表面の粒界及び粒界近傍のガラス質が優先的に腐食されて窒化ケイ素の柱状粒子が残り、微細な凹凸が形成され且つ表面の窒化ケイ素の面積率が増加するため、基材表面の熱膨張係数がダイヤモンドに一层近くなり、高い密着性が得られることが記載されている。

## 【0008】

【発明が解決しようとする課題】 しかしながら、上記した従来の方法においても、セラミックス焼結体とダイヤモンド又はダイヤモンド状炭素被膜との密着性を十分に向上させることは難しかった。即ち、窒化アルミニウムや炭化チタン等の中間層を設ける方法では、中間層の形成によって被覆回数と被膜数を増加させることになり、中間層相互の間及び中間層とダイヤモンド又はダイヤモンド状炭素の被膜との間で剥離が生じる可能性が高くなる。

【0009】 又、セラミックス焼結体を酸又はアルカリで処理する方法では、表面の微細な凹凸形状に沿ってダイヤモンド又はダイヤモンド状炭素の被膜を形成することが難しく、且つ粒界のガラス相が溶け出して形成された空孔内部に被膜が十分に回り込まず、従って期待されるほどの密着性の向上が得られない。

【0010】 更に、セラミックス焼結体を酸又はアルカリで処理する方法の場合、フッ酸やフッ硝酸あるいは水

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酸化ナトリウム等を用いるので、これらの管理のみならず、安全性や環境面での対応が必要となる。加えて、酸やアルカリによる腐食処理条件も厳密に管理する必要があり、セラミックス焼結体のガラス相が溶け過ぎたり又は溶けなさ過ぎたりした場合には、密着性の低下を来し、これにより歩留りの減少を引き起こす可能性がある。

【0011】本発明は、かかる従来の事情に鑑み、セラミックス焼結体の表面に密着性に優れたダイヤモンド又はダイヤモンド状炭素の被膜を備えたセラミックス製摺動部材を提供すること、及びかかるセラミックス製摺動部材を簡単な方法で、生産性良く、且つ高い歩留りで形成する方法を提供することを目的とする。

【0012】

【課題を解決するための手段】上記目的を達成するため、本発明が提供するセラミックス製摺動部材は、窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体の表面上に、ダイヤモンド又はダイヤモンド状炭素の被膜を設けたセラミックス製摺動部材であって、該被膜の設けられたセラミックス焼結体の表面から少なくとも100 $\mu$ mの深さの領域内のCa濃度が、この領域より内部におけるCa濃度よりも減少していることを特徴とする。

【0013】本発明のセラミックス製摺動部材の製造方法は、窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体を真空中において熱処理することにより、セラミックス焼結体の表面から少なくとも100 $\mu$ mの深さの領域内のCa成分を消失ないし減少させ後、その表面にダイヤモンド又はダイヤモンド状炭素の被膜を形成することを特徴とする。

【0014】尚、ここで言うダイヤモンド状炭素とは、非晶質でダイヤモンドと類似の特性を有する炭素を意味し、英語ではDiamond-like carbonと称するものである。

【0015】

【作用】本発明においては、窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体の原料である窒化ケイ素粉末に含まれる微量の不純物、特にカルシウム化合物に着目し、焼結体表面ないしその近傍からカルシウム化合物を消失ないし減少させることにより、セラミックス焼結体とダイヤモンド又はダイヤモンド状炭素の被膜との密着性を向上させることができた。

【0016】即ち、窒化ケイ素( $\text{Si}_3\text{N}_4$ )又はサイアロン( $\text{SiAlON}$ )を主成分とするセラミックス焼結体は、その目的とする用途に応じて、適切な粒径、純度、 $\alpha$ 率、アスペクト比等を有する市販の窒化ケイ素粉末を用い、これに焼結助剤を添加混合して焼結することにより製造されるが、窒化ケイ素粉末には $\text{Si}_3\text{N}_4$ 以外に微量の不純物、例えば酸素、炭素、塩素、鉄、カルシウム、アルミニウム等が含まれている。

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【0017】これらの不純物は、窒化ケイ素粉末を作製する際に使用する設備や治具等から混入するものであったり、窒化ケイ素粉末を作製するための原料としての固体や液体に既に含まれているものであって、これを全て完全に無くすることは極めて困難である。

【0018】従って、窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体は、これらの不純物を含んでおり、その表面及び内部についてX線解析を行うと、いずれの箇所にも $\text{Y}_{20}\text{N}_4\text{Si}_{12}\text{O}_{48}$ と $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$ が形成されていることが判明した。又、このセラミックス焼結体を真空中で熱処理すると、焼結体内部にはこれらの化合物が残っているが、焼結体表面では $\text{Y}_{20}\text{N}_4\text{Si}_{12}\text{O}_{48}$ のみが残り、 $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$ は消失することが分かった。

【0019】そこで、予め真空中で熱処理したセラミックス焼結体と、かかる熱処理を行わないセラミックス焼結体について、それぞれ表面にダイヤモンド被膜及びダイヤモンド状炭素被膜を形成し、その密着性をピン-オン-ディスク試験方法により評価したところ、予め真空中で熱処理したセラミックス焼結体は熱処理無しの焼結体に比べて約3倍の密着性を示した。

【0020】この理由は明らかではないが、以下のごとく考えることができる。CaとMgは表1に示すように、酸素との結合においてイオン結合性がSiよりも高く、また結合力も弱い。従って、真空中で熱処理するとセラミックス焼結体表面からイオン結合性の高いCaとMgが消失するため、焼結体表面近傍はイオン結合性が弱くなり、共有結合性が高くなる。

【0021】

【表1】

| 元素 | イオン結合性(%) | 単結合の強さ(kJ/mol) |
|----|-----------|----------------|
| Si | 37        | 444            |
| Ca | 62        | 134            |
| Mg | 55        | 155            |

【0022】又、ダイヤモンド及びダイヤモンド状炭素は共に $\text{sp}^3$ 混成軌道であり、共有結合性を示すことが知られている。このために、共有結合性を示すダイヤモンド又はダイヤモンド状炭素の被膜は、共有結合性の高い焼結体表面にイオン結合性を示す焼結体表面よりも強く結合することにより、密着性に優れた被膜の形成が可能になったものと考えられる。

【0023】尚、窒化ケイ素又はサイアロンを主成分とする焼結体に真空中で熱処理を施した後、焼結体中の $\text{Y}_{20}\text{N}_4\text{Si}_{12}\text{O}_{48}$ と $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$ の元素分析の評価と、ダイヤモンド又はダイヤモンド状炭素の被膜の密着性をピン-オン-ディスク試験法で評価した結果、真空中で熱処理した場合の密着性が熱処理しない場合の密着性よりも優れているためには、 $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$ の濃度分布、即ちCa成分の濃度分布が焼結体の表面から少なくとも100 $\mu$ mの深さの領域か

ら減少している必要があることが分かった。

【0024】かかるCa成分の消失ないし減少に基づくダイヤモンド又はダイヤモンド状被膜の密着性の向上を得るための真空中での熱処理は、好ましくは $10^{-3}$  Pa以下の真空中で行う。熱処理時の雰囲気圧が $10^{-3}$  Paを越える圧力の場合には、焼結体表面に酸化膜が形成され、熱処理によってもCaやMg成分が焼結体表面から散逸することが困難になるため、本発明の効果が期待できなくなる。

【0025】真空中での熱処理の条件は1100～1400℃の温度で2～6時間行うことが好ましい。この条件が1100℃未満の温度又は2時間未満の熱処理時間では焼結体表面が効果的に改質されず、ダイヤモンド又はダイヤモンド状炭素被膜の密着性が十分向上しない。逆に、1400℃を越える温度又は6時間を越える熱処理時間では、窒化ケイ素が昇華する恐れがあるからである。

【0026】又、この真空中での熱処理を施すことにより、窒化ケイ素又はサイアロンを主成分とする焼結体の粒界相を結晶化させることが可能であり、その場合には必要に応じて熱処理の温度と時間のパターンを調整すれば良い。この熱処理による粒界相の結晶化によって、焼結体の高温での強度が向上する。

【0027】かかる本発明において、セラミックス焼結体は窒化ケイ素又はサイアロンを主成分とするセラミックスであり、他のセラミックス成分、例えば炭化ケイ素(SiC)、ジルコニア( $ZrO_2$ )、炭化チタン(TiC)、炭化ハフニウム(HfC)等が含まれていても構わない。又、炭化ケイ素ウイスカー、窒化ケイ素ウイスカー、カーボンウイスカー等のウイスカーを含むものであっても良い。

【0028】窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体の粉末原料には前記のごとく不純物が含まれ、その含有量は直接窒化法やイミド分解法等の窒化ケイ素粉末の製造方法又は粉末の精練方法等によって異なる。特にCaの含有量については、市販の窒化ケイ素粉末で0.5ppm～2重量%程度であるが、本発明の効果を達成するためには不純物のCa含有量が1ppm～1重量%の範囲にあることが好ましい。焼結体中のCa含有量が1ppm以上である場合に本発明の真空中熱処理による被膜の密着性向上効果が顕著になり、1重量%を越えると摺動部材として十分緻密な焼結体が得られなくなるからである。

【0029】窒化ケイ素又はサイアロンを主成分とする\*

#### 窒化ケイ素粉末の性状

| メジアン径      | 不純物含有量 |        |        |        |       |       |         |
|------------|--------|--------|--------|--------|-------|-------|---------|
| ( $\mu$ m) | Al     | O      | C      | Ca     | Fe    | Cl    | Mg      |
| 0.9        | 20ppm  | 1.2wt% | 0.1wt% | 0.2wt% | 20ppm | 15ppm | 0.01wt% |

【0035】この混合粉末を乾燥した後、5000kg/cm<sup>2</sup>の圧力でCIP成形した。得られた成形体を1

\*セラミックス焼結体の製造には、窒化ケイ素粉末に焼結助剤を添加して焼結するが、本発明のセラミックス焼結体はその焼結助剤を含有し得ることは当然である。かかる焼結助剤としては、例えば酸化イットリウム( $Y_2O_3$ )、酸化アルミニウム( $Al_2O_3$ )、窒化アルミニウム(AlN)、酸化ジルコニウム( $Zr_2O_3$ )、酸化マグネシウム(MgO)、酸化エルビウム( $Er_2O_3$ )、酸化ジスプロシウム( $Dy_2O_3$ )、酸化チタン( $TiO_2$ )、酸化ケイ素( $SiO_2$ )、酸化イッテルビウム( $Yb_2O_3$ )等を挙げることができる。

【0030】セラミックス焼結体の大きさは限定されず、形状についても円柱状、棒状、中空状、細孔部を有する形状、その他いかなる複雑な形状を有するものでも良い。かかるセラミックス焼結体は、被膜の形成に先立って、使用目的に応じて研磨、ラッピング処理等を施すこともできる。

【0031】上記真空中での熱処理を施した窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体の表面上に、ダイヤモンド又はダイヤモンド状炭素の被膜を形成するには、公知のあらゆる方法を使用できるが、なかでも各種CVD法、燃焼法、イオンプレーティング法、スパッタリング法等の気相合成法を用いることが実用上及び生産上において好ましい。

【0032】具体的には、気相合成法は炭素源ガスを含む原料ガスを反応室内で励起させ、焼結体上にダイヤモンド又はダイヤモンド状炭素の被膜を形成させる。炭素源ガスとしては、各種炭化水素のほか、窒素、ハロゲン、酸素等を含む炭素化合物、あるいはこれらの混合物を用い、必要に応じて水素、アルゴン、ヘリウム等と混合して使用する。原料ガスの励起方法としては、RFプラズマCVD法、DCプラズマCVD法、マイクロ波プラズマCVD法、熱フィラメントCVD法、熱CVD法、プラズマフラッシュ法、熱プラズマ法がある。

【0033】

【実施例】

#### 実施例1

下記表2に示す粒径(中央値であるメジアン径)と不純物含有量をもつ市販の $Si_3N_4$ 粉末を使用し、これに平均粒径1.1 $\mu$ mの $Y_2O_3$ 粉末5重量%と平均粒径0.6 $\mu$ mの $Al_2O_3$ 粉末3重量%を添加し、エタノール中で100時間ボールミルによる湿式混合を行った。

【0034】

【表2】

気圧の窒素ガス雰囲気中にて1600℃で4時間加熱保持し、次に1700℃で6時間の焼結を行い、得られた

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焼結体に1700℃、500気圧の窒素ガス雰囲気中に2時間のHIP処理を施した。

【0036】かくして得られた窒化ケイ素焼結体をラッピング処理した後、真空熱処理炉内に配置した。次に、炉内を $10^{-3}$ Paに真空排気し、試験片を1300℃に3.5時間保持する真空熱処理を施した。この真空熱処理を施した焼結体の表面に、RFプラズマCVD法を用いて厚さ1.1μmのダイヤモンド状炭素被膜を形成し、試験片1とした。ダイヤモンド状炭素被膜の成膜条件は、原料ガスとしてメタンガスを用い、圧力0.5 Torrで、出力電力800Wとした。

【0037】又、比較のために、上記と同様に製造した窒化ケイ素焼結体をラッピング処理した後、真空中で熱処理する代わりに窒素雰囲気中で熱処理を行いダイヤモンド状炭素被膜を形成した比較試験片1aと、真空熱処理を行わず、同じ条件でダイヤモンド状炭素被膜を形成した比較試験片1bと、ラッピング処理のみを行い、ダイヤモンド状炭素被膜を有しない比較試験片1cとを作製した。尚、窒素雰囲気中での熱処理条件は、真空中の場合と同じ1300℃で5時間とし、大気圧で処理を行った。

【0038】これらの試験片1及び比較試験片1a、1b、1cを用いて、ピン-オン-ディスク試験方法に従い、荷重20N、摺動速度150mm/秒、摺動回数50000回の条件で摺動試験を行った。その結果、摩擦係数は、ダイヤモンド状炭素被膜のない比較試験片1cでは0.9であったが、本発明の試験片1、窒素雰囲気中で熱処理した試験片1a、及び熱処理を行わずにダイヤモンド状炭素被膜を形成した比較試験片1bは共に0.2であった。

【0039】ところが、摩擦深さをみると、比較試験片1cが8μm、比較試験片1a及び1bが3μmであるのに対して、本発明の試験片1では0.8μmと遥かに少なかった。又、窒素雰囲気中で熱処理した後に被膜形成した比較試験片1a、熱処理なしに被膜形成した比較試験片1bでは、ダイヤモンド状炭素被膜の剥離が認められたが、本発明の試験片1には被膜の剥離は認められなかった。これらの結果から、真空熱処理の後にダイヤモンド状炭素被膜を形成した本発明の試験片1では、被膜の密着性が著しく向上することが判明した。

【0040】一方、上記と同じ窒化ケイ素焼結体であって、本発明に従って真空中で熱処理を施した焼結体と、窒素雰囲気中で熱処理を施した焼結体及び熱処理を施していない焼結体について、X線マイクロアナライザー(EPMA)を用いて粒界相中の元素分布を深さ方向について調べ、結果を図1に示した。図1は、焼結体表面から深さ方向における $Y_{2.0}N_4Si_{1.2}O_{4.8}$ と $Ca(Fe, Mg)Si_2O_6$ の分布を示すグラフであり、縦軸は

窒化ケイ素粉末の性状

メジアン径

不純物含有量

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真空熱処理を施した焼結体における表面での $Y_{2.0}N_4Si_{1.2}O_{4.8}$ の含有量を100とした相対目盛で表示してある。

【0041】図1から分かるように、窒素雰囲気中で熱処理を施した焼結体及び熱処理を施していない焼結体は、 $Y_{2.0}N_4Si_{1.2}O_{4.8}$ 及び $Ca(Fe, Mg)Si_2O_6$ が共に深さ方向に対して一定の分布になっており、窒素雰囲気中での熱処理が効果がないことが判明した。これに対して、真空中で熱処理を施した焼結体では、内部には両方の化合物が存在しているものの、 $Ca(Fe, Mg)Si_2O_6$ は表面から約400μmの深さから表面に向かって徐々に減少を始め、表面では全く検出されなかった。

【0042】又、実施例1と同じ焼結体からなる抗折試験片を用いて、上記と同じ条件で真空中での熱処理又は窒素雰囲気中での熱処理を行い、これらの試験片と熱処理を行っていない試験片にラッピング処理後同じ条件でプラズマCVD法により1.1μmのダイヤモンド状炭素被膜を形成した。

【0043】これらのダイヤモンド状被膜を設けた各試験片を用いて、常温、600℃、800℃、900℃、1000℃、1100℃、1200℃、1300℃での抗折力を測定した。その結果を図2に示す。この結果から分かるように、真空中での熱処理を行った試験片は高温においても最も抗折力の劣化が小さく、窒素雰囲気中での熱処理を行った試験片は熱処理を施していないものと余り変わらない温度依存性を示した。

【0044】更に、これら各試験片の結晶構造回折を調べると、真空中での熱処理を行った試験片には窒化ケイ素のパターン以外に結晶質の粒界相に起因するピークが現れているが、窒素雰囲気中で熱処理した試験片では窒化ケイ素のパターン以外は僅かしか結晶質の粒界相によるピークが現れていなかった。又、熱処理を行っていない試験片では窒化ケイ素のピークのみが検出された。これらの結果より、真空中で熱処理を行うことにより、ダイヤモンド状炭素被膜の密着性が向上するばかりでなく、粒界相の結晶化により高温特性をも向上させることができる。

#### 【0045】実施例2

下記表3に示す粒径(中央値であるメジアン径)と不純物含有量をもつ市販の $Si_3N_4$ 粉末を使用し、これに平均粒径0.8μmの $Er_2O_3$ 粉末6重量%、平均粒径1.1μmのAlN粉末3重量%、短径0.4~2μmで長さ5~50μmのSiCウイスカー10重量%を添加し、実施例1と同様に湿式混合し、乾燥した。

【0046】

【表3】

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| ( $\mu\text{m}$ ) | Al    | O      | C      | Ca     | Fe    | Cl    | Mg      |
|-------------------|-------|--------|--------|--------|-------|-------|---------|
| 1.5               | 30ppm | 2.1wt% | 0.1wt% | 0.6wt% | 60ppm | 29ppm | 0.01wt% |

【0047】この混合粉末を200気圧、1750℃、2時間の条件でホットプレス焼結を行い、窒化ケイ素焼結体を製造した。かくして得られた窒化ケイ素焼結体をラッピング処理した後、真空熱処理炉内に配置し、炉内を $10^{-4}$  Paに真空排気して1400℃で2.5時間の真空熱処理を行った。

【0048】この真空熱処理を施した焼結体の表面に、RFプラズマCVD法を用いて厚さ0.6  $\mu\text{m}$ のダイヤモンド状炭素被膜を形成し、本発明の試験片2とした。このダイヤモンド状炭素被膜の成膜条件は、原料ガスとしてメタンガスを用い、圧力0.8 Torrで、出力電力600Wとした。

【0049】又、比較のために、上記と同様に製造した窒化ケイ素焼結体をラッピング処理した後、真空熱処理を行わず、同じ条件でダイヤモンド状炭素被膜を形成した比較試験片2aと、ラッピング処理のみを行い、ダイヤモンド状炭素被膜を形成しない比較試験片2bとを作製した。

【0050】これらの試験片2及び比較試験片2a、2bを用いて、実施例1と同様の条件で摺動試験を行った。その結果、摩擦係数は、ダイヤモンド状炭素被膜のない比較試験片2bでは1.3であったが、本発明の試験片2及び真空熱処理を行わずに被膜形成した比較試験片2aは共に0.2であった。

【0051】ところが、摩擦深さをみると、比較試験片2bが9  $\mu\text{m}$ 、比較試験片2aが2  $\mu\text{m}$ であるのに対して、本発明の試験片2は0.4  $\mu\text{m}$ と遥かに少なく、しかも真空熱処理なしに被膜形成した比較試験片2aではダイヤモンド状炭素被膜の剥離が認められたが、本発明の試験片2には被膜の剥離は認められなかった。これらの結果から、真空熱処理の後にダイヤモンド状炭素被膜を形成した本発明の試験片2では、被膜の密着性が著しく向上していることが判明した。

### 【0052】実施例3

実施例2と同様にして製造した窒化ケイ素焼結体を研削加工した後、真空熱処理炉内に配置し、炉内を $10^{-4}$  Pa\*

#### 窒化ケイ素粉末の性状

| 粉末種類 | メジアン径( $\mu\text{m}$ ) | 不純物含有量  |
|------|------------------------|---|
|      |                        | Al O C Ca Fe Cl Mg                              |
| A    | 0.7                    | 30ppm 2.5wt% 0.1wt% 0.1wt% 50ppm 18ppm 0.01wt%  |
| B    | 0.7                    | 28ppm 2.6wt% 0.13wt% 1.5wt% 47ppm 18ppm 0.01wt% |

【0057】この混合粉末を乾燥した後、5000 kg/cm<sup>2</sup>の圧力でCIP成形した。得られた成形体を1気圧の窒素ガス雰囲気中にて1600℃で4時間加熱保持し、次に1800℃で5時間の焼結を行い、得られた焼結体に1750℃、1000気圧の窒素ガス雰囲気中にて2時間のHIP処理を施した。

【0058】かくして得られた各窒化ケイ素焼結体の組

\* aに真空排気して1200℃で4時間の真空熱処理を行った。この真空熱処理を施した焼結体の表面に、RFプラズマCVD法を用いて厚さ5  $\mu\text{m}$ のダイヤモンド被膜を形成し、ピン-オン-ディスク試験片3aを作製した。又、比較のために、上記と同様に製造した窒化ケイ素焼結体を研削加工した後、真空熱処理を行わずに、同じ条件でダイヤモンド被膜を形成した比較試験片3bを作製した。

【0053】これらの試験片3a、3bを用いて、実施例1及び2と同様の摺動試験を行った。その結果、本発明による試験片3aではダイヤモンド被膜の剥離が認められなかったが、比較試験片3bでは大きな剥離が見られた。この結果から、真空熱処理の後にダイヤモンド被膜を形成した本発明の試験片3aでは、被膜の密着性が向上していることが分かった。

【0054】又、これらの試験片3a、3bについて、焼結体の表面から深さ方向におけるY<sub>2</sub>O<sub>3</sub>N<sub>4</sub>Si<sub>12</sub>O<sub>48</sub>とCa(Fe, Mg)Si<sub>2</sub>O<sub>6</sub>の分布を、実施例1と同様にして測定した。その結果、本発明の試験片3aの内部には両方の化合物が存在しているものの、Ca(Fe, Mg)Si<sub>2</sub>O<sub>6</sub>は表面から約350  $\mu\text{m}$ の深さから表面に向かって徐々に減少を始め、表面では全く検出されなかった。一方、比較試験片3bでは、両方の化合物共に深さ方向に対して一定の分布になっていることが判明した。

### 【0055】実施例4

下記表4に示す粒径(中央値であるメジアン径)と不純物含有量をもつ2種類の市販のSi<sub>3</sub>N<sub>4</sub>粉末を使用し、各々のSi<sub>3</sub>N<sub>4</sub>粉末に平均粒径0.8  $\mu\text{m}$ のAl<sub>2</sub>O<sub>3</sub>粉末4重量%、平均粒径1.0  $\mu\text{m}$ のAlN粉末4重量%、平均粒径0.8  $\mu\text{m}$ のY<sub>2</sub>O<sub>3</sub>粉末3重量%を添加して、エタノール中で100時間ボールミルによる湿式混合を行った。

### 【0056】

【表4】

組織観察及び密度を測定すると、粉末Aを用いた焼結体は欠陥が無く、密度は3.24 g/cm<sup>3</sup>であり十分緻密化していることが分かった。しかし、粉末Bを用いた焼結体は表面や内部にボア等の欠陥が多く、密度も3.11 g/cm<sup>3</sup>と十分緻密化していなかった。

【0059】次に、この粉末Aを用いて製造した焼結体をピン-オン-ディスク試験用に加工し、ラッピング処

理した後、真空熱処理炉内に配置して炉内を $10^{-3}$  Paに真空排気し、試験片を $1150^{\circ}\text{C}$ にて下記表5に示す時間条件で保持することにより、真空熱処理を施した。この場合、条件5の $1150^{\circ}\text{C}$ で8時間の真空熱処理を行った試験片は、表面付近の窒化ケイ素が昇華しており、熱処理前の試験片の形状を保持していなかった。

【0060】条件1から条件4までの真空熱処理を施した試験片の表面に、RFプラズマCVD法を用いて厚さ $1.5\mu\text{m}$ のダイヤモンド状炭素被膜を形成した。これ\*

|                           | 条件1 | 条件2 | 条件3  | 条件4  | 条件5 |
|---------------------------|-----|-----|------|------|-----|
| 保持時間(H)                   | 0.5 | 1.0 | 2.0  | 5.0  | 8.0 |
| 摩擦係数                      | 0.9 | 0.8 | 0.3  | 0.2  | —   |
| 摩耗深さ( $\mu\text{m}$ )     | 2.7 | 2.6 | 0.8  | 0.8  | —   |
| 被膜の状態                     | 剥離  | 剥離  | 剥離無し | 剥離無し | —   |
| Ca濃度低下起点( $\mu\text{m}$ ) | 30  | 80  | 110  | 340  | —   |

(注) 条件5では表面付近の窒化ケイ素が昇華した。

【0062】これらの結果から、条件1及び2のように焼結体表面より $100\mu\text{m}$ 以上深い箇所からCa濃度が低下していない場合には、ダイヤモンド状炭素被膜が剥離しているのに対して、条件3及び4のように焼結体表面より $100\mu\text{m}$ 以上深い箇所からCa濃度が低下している場合は、ダイヤモンド状被膜の剥離が生じず、被膜の密着性が向上していること、及び摩耗深さも条件1及び2に比べて小さくなっていることが分かる。

【0063】

【発明の効果】本発明によれば、窒化ケイ素又はサイアロンを主成分とするセラミックス焼結体の表面に、高い密着性のダイヤモンド又はダイヤモンド状炭素の被膜を簡単な方法で、生産性良く、且つ高い歩留りで形成することができ、従って表面に高い密着性のダイヤモンド又

\*らの試験片を実施例1と同様の条件でピンオンディスク試験を行い、その摩擦係数及び摩耗深さを評価した結果を表5に併せて示した。又、これらの試験片を試験面に垂直に切断し、試験面からの深さ方向に対するCa成分の濃度変化をEPMAにより測定し、その結果を図3に示すと共に、Ca濃度が低下する起点の表面からの深さを求めて表5に示した。

【0061】

【表5】

はダイヤモンド状炭素の被膜を備えたセラミックス製摺動部材を提供することができる。

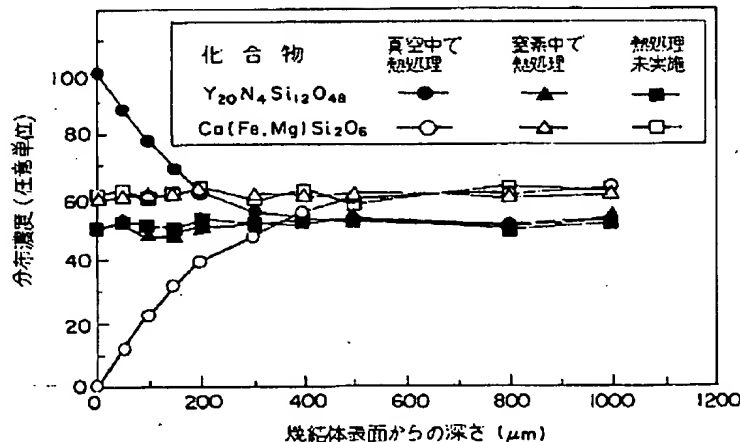
【図面の簡単な説明】

【図1】実施例1での熱処理条件の異なる焼結体ごとに、焼結体表面から深さ方向における $\text{Y}_{20}\text{N}_4\text{Si}_{12}\text{O}_{48}$ と $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$ の濃度分布を示したグラフである。

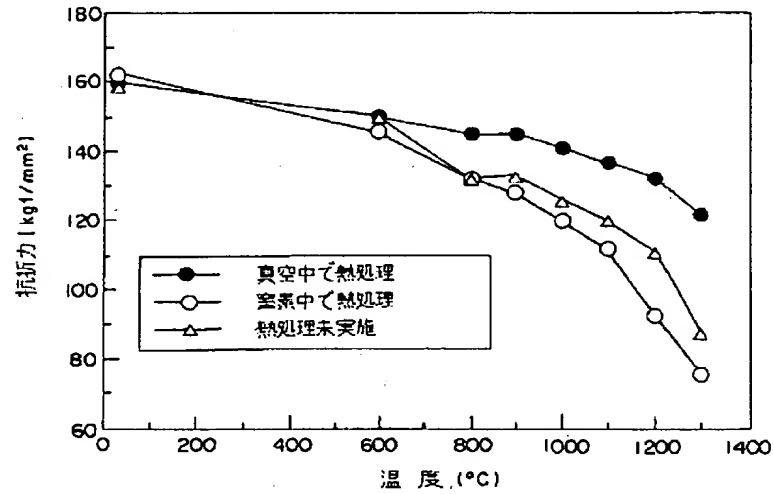
【図2】実施例1での熱処理条件の異なる焼結体ごとに、焼結体の抗折力と測定温度との関係を示したグラフである。

【図3】実施例4での熱処理条件の異なる焼結体ごとに、焼結体表面から深さ方向における $\text{Ca}(\text{Fe}, \text{Mg})\text{Si}_2\text{O}_6$ の濃度分布を示したグラフである。

【図1】



【図2】



【図3】

